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Author(s)	Yamaguchi, Seira; Nakamura, Kyotaro; Masuda, Atsushi; Ohdaira, Keisuke
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Description	

Rapid progression and subsequent saturation of polarization-type potential-induced degradation of n-type front-emitter crystalline-silicon photovoltaic modules

Seira Yamaguchi[1]*, Kyotaro Nakamura[2], Atsushi Masuda[3], and Keisuke Ohdaira[1]

[1] *Japan Advanced Institute of Science and Technology, Nomi, Ishikawa 923-1292, Japan*
[2] *Meiji University, Kawasaki, Kanagawa 214-8571, Japan*
[3] *National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8568, Japan*

In this study, we investigated progression of potential-induced degradation (PID) in photovoltaic modules fabricated from n-type-based crystalline-silicon cells with front p$^+$ emitters. In PID tests in which a bias of −1000 V was applied to the modules, they started to degrade within 5 s and their degradation saturated within 60 s. This behavior suggested that the PID was caused by positive charge accumulation in the front passivation films. Performing PID tests with a bias of −1500 V revealed that the degradation rate strongly depended on the applied bias whereas the saturation value was independent of the applied bias. Regeneration tests on degraded modules previously subjected to PID tests for durations of 5 and 10 min were performed by applying a positive bias of +1000 V. All the degraded modules completely recovered their performance losses within 60 s regardless of the degradation test duration. On the basis of these results, we proposed that these positive charges originate from positively charged K centers formed by extracting electrons from neutral and negatively charged K centers. This model readily explains the observed degradation and regeneration behavior. To test our model, we determined the fixed positive charge densities (Q_f) of a silicon nitride passivation film before and after PID, for which it was found that Q_f showed similar saturation behavior. Additionally, the saturated Q_f value was of the same order as K center density. These results support our model involving a charging process of K centers.

1. Introduction

Recently, n-type front-emitter (FE) crystalline-silicon (c-Si) photovoltaic (PV) cells including passivated emitter rear totally diffused (PERT) cells and passivated emitter and rear cells (PERCs) have attracted attention because of their potential to achieve higher efficiencies than those of conventional p-type c-Si PV cells.[1–4] These n-type c-Si PV cells have high-quality n-type base materials, where the minority carrier lifetimes are generally long because of the small impurity capture cross sections for minority carriers;[5] this leads to high energy conversion efficiencies. In addition, the stability of these cells is expected to favor their long-term

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[*] E-mail: s-yamaguchi@jaist.ac.jp

use because they are known not to suffer much from light-induced degradation (LID). LID is frequently observed in conventional p-type c-Si PV cells and is caused by the formation of metastable boron–oxygen complexes.[6,7] Consequently, n-type FE c-Si PV cells may display superior long-term stability over p-type ones and may therefore be suitable for use in large-scale PV systems.

However, to use PV cells in large-scale PV systems, it is very important to understand the mechanism of their potential-induced degradation (PID).[8–11] In large-scale PV systems, there are large electric-potential differences between the active circuit and the grounded frame of modules, particularly near either end of a module string. These differences may lead to marked performance loss of PV modules, called PID. PID often causes a large performance deterioration over a relatively short term, for example, several months; therefore, it is considered one of the most important reliability issues of large-scale PV systems.

There have been multiple previous studies on PID of n-type Si-wafer-based PV cell modules.[12–25] As for n-type FE c-Si PV modules, Hara et al.[12] reported that polarization-type PID (PID-p), characterized by decreases in short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}), occurs under negative bias. Additionally, they proposed that the PID is caused by enhanced surface recombination induced by an increase in the positive charge density within the front silicon nitride (SiN_x) passivation layers. This mechanism is similar to that proposed by Swanson et al.,[13] who investigated PID-p in n-type interdigitated back-contact (IBC) c-Si PV modules. The proposed model was experimentally confirmed by Bae and coworkers, who reported increased positive charge density in a SiN_x film after a PID test.[14] Moreover, Hara and colleagues have clearly shown that PID in n-type FE c-Si PV modules is a very serious issue because it readily occurs at room temperature or under a very low bias of −50 V.[12] This indicates that PID-p can occur even in small-scale PV systems with relatively low system bias.

It is also important to clarify the time dependence of this kind of PID, which may increase our understanding of not only the time dependence itself but also the mechanism of PID. However, a detailed time-dependent analysis of PID has not yet been reported. Moreover, the origin of additional positive charges in SiN_x films has not yet been identified. In our recent work,[15] PID was found to occur rapidly and strongly saturate, for example, within several minutes in a PID test, and a model to describe the progression and saturation behaviors was presented.

Here, we report and discuss our obtained results in greater detail than in our previous publication.[15] In our previous study,[15] we used commercially available n-type PERT cells as

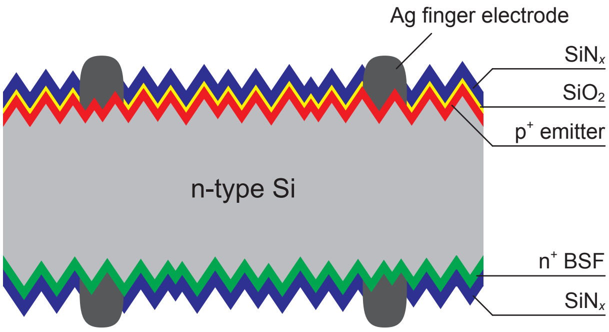

Fig. 1. Schematic diagram of the n-type PERT cells used in this study (not to scale). The cells had Cu busbars on both sides (not shown in this figure).

n-type FE c-Si solar cell samples. In this study, we use different n-type PERT cells that we fabricate ourselves and whose structure is therefore known. We first report the progression and saturation behaviors of PID in the initial stage observed in an acceleration test of PV modules fabricated using cells with a front p$^+$ emitter and silicon dioxide (SiO_2) and SiN_x front passivation stack. We measure the applied bias dependence of their degradation behavior and present the results of regeneration tests of degraded PV modules. On the basis of our results, we propose a model that can explain the observed degradation behavior, and we test the model by additional experiments. In this study, we use n-type PERT cell modules as test samples; however, the findings can be applied to PID in other kinds of PV modules with cells that have a similar front structure; for example, PERCs. Additionally, our findings may be extended to PID in IBC c-Si PV modules because their degradation mechanisms are considered to be very similar to those of PERT modules.

2. Experimental procedure

We used n-type PERT cells as n-type FE c-Si PV cell samples. (Note that the cells were different from the commercial cells used in our previous study.[15]) The cell structure is schematically illustrated in Fig. 1. These cells contained front boron emitters and phosphorus back-surface fields (BSFs). The emitters were passivated with stacks composed of a SiN_x layer prepared by plasma-enhanced chemical vapor deposition (PECVD) and an underlying thermally grown SiO_2 layer. The BSFs were passivated with a single-layer SiN_x film formed by PECVD. The cells had screen-printed grid electrodes composed of copper (Cu) busbars and silver (Ag) fingers on both sides. The cells were cleaved into pieces with dimensions of 20×20 mm and standard interconnector ribbons were soldered onto the busbars on both sides. After soldering, we prepared stacks composed of conventional tempered cover glass/ethylene–vinyl acetate copolymer (EVA) sheet/cell/EVA sheet/typical white backsheet. PV modules were prepared by laminating the stacks in a module laminator. Our lamination process consisted of a degassing step for 5 min and an adhesion step for 15 min. The stacks were placed on a stage maintained at 135 °C during both steps.

PID tests were performed by applying a negative bias of −1000 V with respect to an aluminum (Al) plate placed on the cover glass of the modules in a chamber maintained at 85 °C. The humidity was not controlled; however, the relative humidity in a similar setup was very low (<2%).26) Therefore, the influence of moisture ingress was disregarded in the tests.

To evaluate cell degradation, current density–voltage (J–V) measurements in the dark and under one-sun illumination were performed before and after the PID tests. From the J–V data obtained under one-sun illumination, we determined J_{sc}, V_{oc}, fill factor (FF), and maximum output power (P_{max}). External quantum efficiency (EQE) measurements were also performed before and after the PID tests. All measurements were conducted at 25 °C.

We performed PID tests where a higher negative bias of −1500 V was applied at 85 °C to clarify how the progression behavior of the PID in the n-type FE c-Si PV modules was influenced by the application of the higher bias. We also conducted regeneration tests on PV modules which were degraded in advance in the above-mentioned PID tests, by applying a positive bias of +1000 V at 85 °C for 5 or 10 min.

To discuss the degradation and saturation mechanism in greater detail, we performed capacitance–voltage (C–V) measurements on 70-nm-thick $\mathrm{SiN}_x/\mathrm{SiO}_2$/p-type c-Si/Al samples using a mercury probe and electron spin resonance (ESR) measurement of a 700-nm-thick SiN_x film deposited on a fused quartz substrate. These SiN_x and SiO_2 films were formed under the same conditions as those used for the fabrication of the complete cells. The $\mathrm{SiN}_x/\mathrm{SiO}_2$/p-type c-Si/Al sample was subjected to C–V measurements before and after a cell-level PID test27,28) under an applied bias of −1000 V at 65 °C to evaluate the change in the charge density (Q_{f}) in the SiN_x film caused by the PID stress. In the ESR measurement, we used the thick SiN_x films to obtain a high signal intensity. We calculated the effective areal K-center density in the SiN_x film with a thickness of 70 nm by dividing the measured areal density by 10. Both the charge density and the K center density were multiplied by the geometry factor 1.73 to take into account the surface texture.

3. Results

It is well known that under negative bias, n-type FE c-Si PV modules undergo PID characterized by decreases in J_{sc} and V_{oc}. Understanding of the progression of device degradation

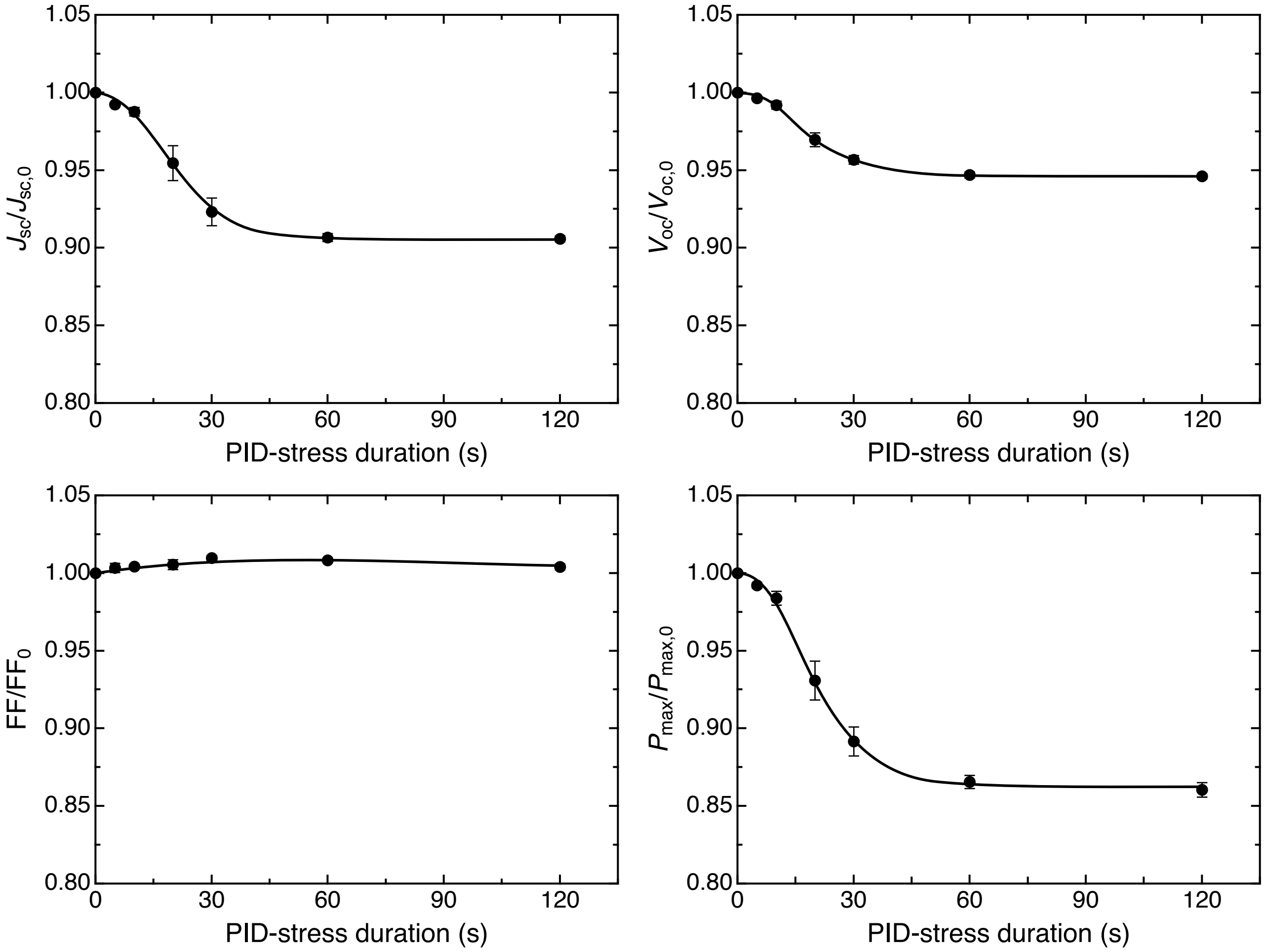

Fig. 2. Dependences of $J_{sc}/J_{sc,0}$, $V_{oc}/V_{oc,0}$, FF/FF$_0$, and $P_{max}/P_{max,0}$ of the n-type c-Si PV modules on the duration of PID stress. The bias and temperature in the PID tests were set to −1000 V and 85 °C, respectively. The data points represent the mean values of three identical modules, and the error bars correspond to the standard deviation of the mean. The solid lines are visual guides.

behavior is always important practically, but a detailed time-dependent analysis of the particular PID in n-type FE PV modules has not yet been performed. In this study, we investigated the progression of PID in the initial stage by performing PID tests in the time range from several seconds to several minutes.

Figure 2 shows the dependences of $J_{sc}/J_{sc,0}$, $V_{oc}/V_{oc,0}$, FF/FF$_0$, and $P_{max}/P_{max,0}$ (the subscript 0 indicates the initial value) of the n-type PERT cell modules on the duration of PID stress. The PID tests were conducted at a negative bias of −1000 V at 85 °C. The parameters were obtained from the *J*–*V* data collected under one-sun illumination. $J_{sc}/J_{sc,0}$ and $V_{oc}/V_{oc,0}$ started to decrease within 5 s and saturated within about 60 s. Comparison with the corresponding *J*–*V* data measured in the dark indicated that diffusion currents were higher after

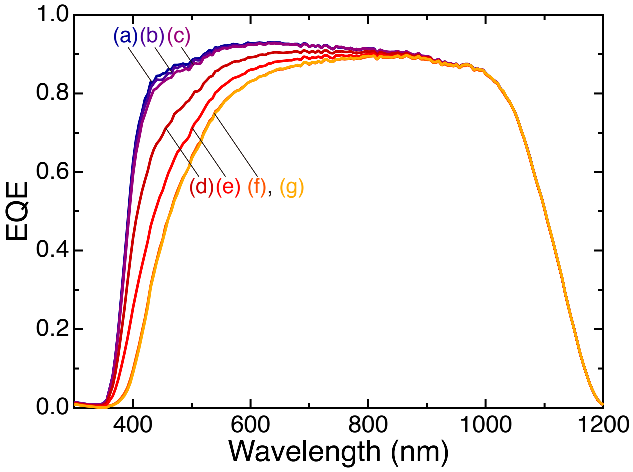

Fig. 3. Representative EQE spectra of the n-type c-Si PV module (a) before and after PID tests for (b) 5, (c) 10, (d) 20, (e) 30, (f) 60, and (g) 120 s. The bias and temperature in the PID tests were set to −1000 V and 85 °C, respectively.

the PID tests (data not shown here). As a result, $P_{\mathrm{max}}/P_{\mathrm{max,0}}$ also rapidly decreased and saturated within 60 s. This result demonstrates that PID in n-type FE c-Si PV modules occurs very rapidly and saturates within a short time.

The EQE spectra of PV modules before and after the PID tests are presented in Fig. 3. For the EQE in the short-wavelength range, very similar decrease and saturation behaviors are seen, which strongly suggest that the decreases in $J_{\mathrm{sc}}/J_{\mathrm{sc,0}}$ and $V_{\mathrm{oc}}/V_{\mathrm{oc,0}}$ accompanied by increased diffusion currents can be attributed to enhanced front-surface recombination. These results also indicate that the rapid degradation and its saturation were caused by a quick increase in front-surface recombination and its saturation.

We investigated the dependence of the progression of PID on applied bias. Figure 4 shows the dependence of the progression of PID in n-type FE c-Si PV modules on applied bias. The degradation rate strongly depended on the applied bias; however, the saturation value of $P_{\mathrm{max}}/P_{\mathrm{max,0}}$ was constant when the applied bias was increased from −1000 to −1500 V.

We also performed regeneration tests on the modules by applying a positive bias of +1000 V. The regenerated modules were subjected to a prior PID test in which a negative bias of −1000 V was applied at 85 °C for 5 or 10 min. The degradation of all the samples was saturated after the PID tests and the saturation values were almost the same. $P_{\mathrm{max}}/P_{\mathrm{max,0}}$ of the modules after the PID tests and subsequent regeneration tests are presented in Fig. 5. All the degraded modules started to regenerate within 5 s and almost completely recovered their performance losses within 60 s. Interestingly, the regeneration behavior was independent of

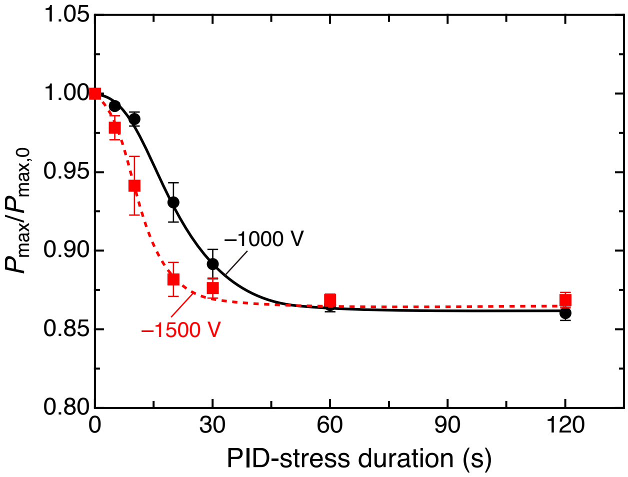

Fig. 4. Applied bias dependence of $P_{max}/P_{max,0}$ of the n-type c-Si PV modules in PID tests. The data points represent the mean values of three identical modules, and the error bars correspond to the standard deviation of the mean. The solid and dashed lines are visual guides.

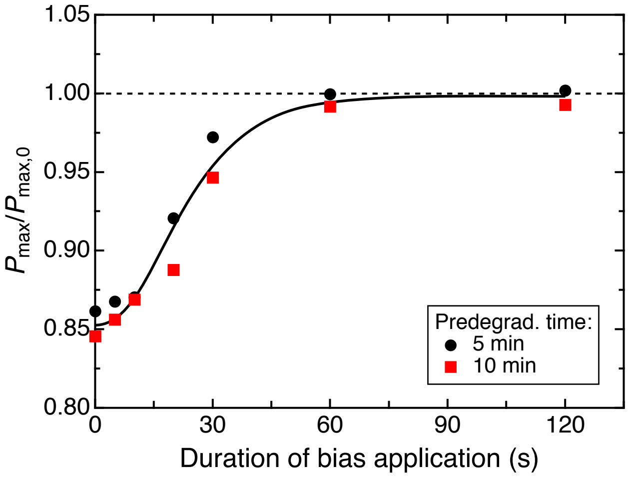

Fig. 5. Regeneration behavior of PV modules degraded in prior PID tests under a negative bias of −1000 V at 85 °C for 5 or 10 min. The regeneration tests were performed by applying a positive bias of +1000 V at 85 °C.

the duration of the degradation test.

4. Discussion

In this study, we investigated the progression of PID in the initial stage in n-type FE c-Si PV modules by performing PID tests for durations ranging from several seconds to several minutes. The results revealed the rapid progression and subsequent saturation of PID, as shown in Fig. 2. The rapid degradation and subsequent saturation were caused by quickly enhanced surface recombination and its saturation. In terms of long-term stability, this may become a very serious issue for actual PV systems. It is also important to understand the mechanism of PID to determine an approach to minimize this effect.

The PID of the n-type FE c-Si PV modules was conspicuously rapid compared with the behavior observed for conventional p-type c-Si PV modules,26) thin-film amorphous Si PV modules,29) n-type rear-emitter c-Si PV modules,16) and Cu(In,Ga)Se_2 (CIGS) thin-film PV modules.26) Naumann et al.30,31) revealed that the PID in conventional p-type c-Si PV modules involves sodium ion (Na^+) migration across the front SiN_x passivation layer. Similarly, it has been proposed that Na^+ migration is related to the PID in n-type rear-emitter c-Si and CIGS PV modules.16,26) However, the rapid PID observed in this study cannot be directly explained by Na^+ migration. This is because the drift time for Na^+ across a SiN_x film with a thickness of 80 nm is on the order of several tens of minutes.32) Therefore, we should consider if the PID is caused by a positive charge accumulation process in the front passivation films, as reported previously.12) Bae et al.14) experimentally confirmed that the density of positive charges in the front SiN_x film of a device increases during a PID test. However, the origin of these additional positive charges is still unknown.

One candidate for the origin of additional positive charges is K centers, which are dangling bonds of Si atoms back-bonded to three nitrogen atoms.33–35) K centers have three different charge states: neutral, positively charged, and negatively charged, which are subsequently referred to as K^0, K^+, and K^- centers, respectively. K centers are known to be present with a typical areal density of $\sim 10^{12}$ cm^{-2} in SiN_x films fabricated by PECVD.36,37) The charge states of K centers can be manipulated via externally applied voltages.36,37) In this context, if electrons are extracted from K^0 and K^- centers by the negative bias applied in the PID tests, the net charge in the passivation films will shift to a more positive value. The additional positive charges that are present because of the extraction of electrons from K centers can explain the observed rapid degradation and subsequent saturation of device performance. Figure 6 shows a schematic diagram of a proposed model involving a charge extraction process from K centers. This model includes some elementary processes (for example, charge transport and electron extraction), although it should be noted that these processes are considered to coincide. Before stressing, K centers exist in the front SiN_x film, as shown in Fig. 6(a). During the application of a negative bias, positive charges accumulate on the surface of the front SiN_x film, as illustrated in Fig. 6(b). These positive charges are limited by the leakage current flowing in the PV module. The positive charges subsequently extract electrons from K^0 and K^- centers, leaving K^+ centers [Fig. 6(c)]. These K^+ centers attract minority carriers, i.e., electrons, and enhance the rate of surface recombination via interface defects. It is possible

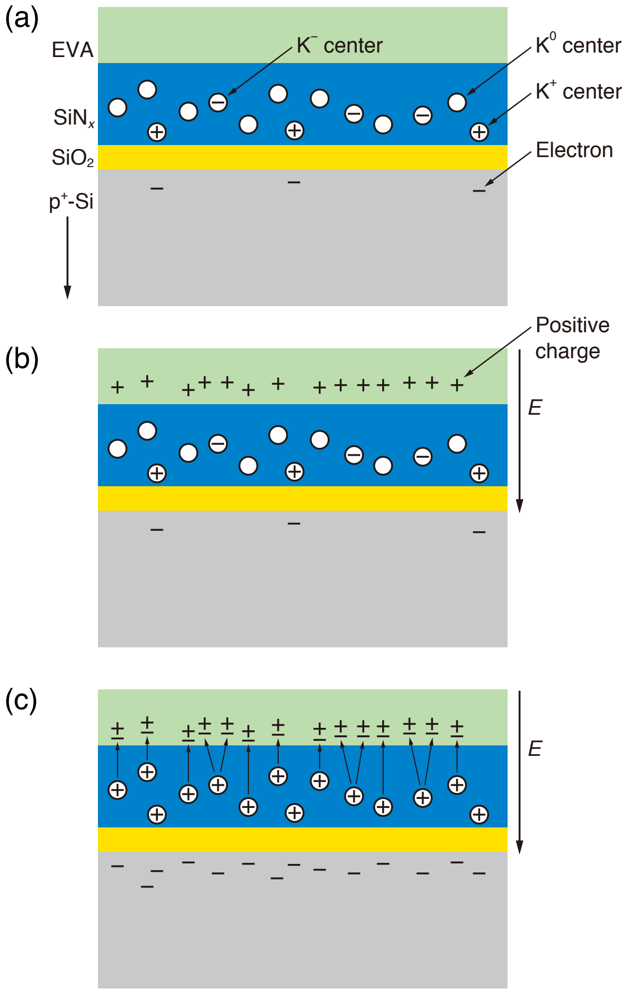

Fig. 6. Schematic diagram of our proposed model for the progression and saturation of PID in n-type c-Si PV modules. Panels (a), (b), and (c) show the cross sections of a PV module near the EVA/cell interface. (a) Before stressing, K centers exist in the front SiN$_x$ film. (b) During application of a negative bias, positive charges accumulate on the surface of the front SiN$_x$ film. (c) The positive charges subsequently extract electrons from K^0 and K$^-$ centers, leaving K$^+$ centers.

that Na$^+$ introduced into the front SiN$_x$ film contributes to the increase in the positive charge density. However, Na$^+$ introduced into the top surface of the front SiN$_x$ film probably has only a small effect on PID because Na$^+$ should exist near the interface with the emitter to exhibit a large effect. As mentioned above, Na$^+$ cannot reach the interface in a short time (within several minutes); thus, its time scale is too large to explain the observed rapid PID. The above model may also be used to explain PID in n-type IBC c-Si PV modules.[13)] In the case of n-type IBC c-Si modules, the terms “negative bias”, “positive charges”, “K$^+$ centers”, and “electrons” should be replaced with “positive bias”, “negative charges”, “K$^-$ centers”, and “holes”, respectively, because their PID occurs under positive bias.

In our model, because the maximum density of positive charges is limited to the total density of K centers, we assume that the saturation of PID occurs when all the K centers are positively charged. On the basis of this reasoning, positive charges exceeding the density of K centers should be supplied within a minute. In this study, a leakage current between the cells and Al plates with ~0.1 μA/cm^2 was observed during the PID tests. This observation indicates that positive charges can accumulate on the front surface of the front SiN$_x$ films with a density of up to approximately 4×10^{13} cm^{-2} in 60 s. This clearly shows that a sufficient number of positive charges to completely charge all the K centers are supplied within a minute, which is consistent with our hypothesis. Note that a part of the currents flowing in the SiN$_x$ films is considered to originate from the extraction of electrons from K centers. After the saturation, currents keep flowing in the samples because there exist other current paths and sources. For example, currents through the front silver electrodes are always flowing during stressing regardless of their current sources, and, furthermore, currents originating from the Na$^+$ drift in the SiN$_x$ films should also be considered. The positive charges originating from Na$^+$ can also contribute to degradation if their density is significantly high. Our model is validated if the density of Na$^+$ is sufficiently lower than that of K$^+$ centers, and our results seem to support the hypothesis that such a situation is realized.

As shown in Fig. 4, the degradation rate strongly depended on the applied bias; in contrast, the saturation value of $P_{\text{max}}/P_{\text{max},0}$ was independent of the applied bias. This applied-bias independence of the saturation value can also be consistently explained by the limited maximum positive charge density. In our model, only the charging rate is increased when the applied bias is increased; the saturation value is unchanged because the maximum number of positive charges is limited by the density of K centers, which is not influenced by applied bias.

In our model, the regeneration process of the PID is explained as a positive-charge release process limited by leakage current. The regeneration process should therefore occur on the same timescale as that of the degradation process that can be explained by the electron extraction process. As shown in Fig. 5, rapid regeneration was observed on the same timescale as that of degradation. Similar leakage current values were observed during the degradation and regeneration tests. Additionally, the regeneration of all samples was completed within 60 s independent of the duration of the degradation test. This implies that in the degradation tests, the positive charge density was already saturated within 60 s, which can be explained by the limited number of positive charges that can accumulate in the front SiN$_x$ layers. This

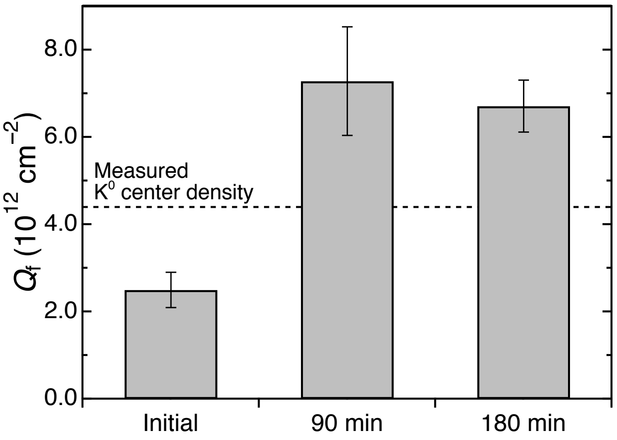

Fig. 7. Variation of Q_f of SiN_x of the test sample undergoing cell-level PID tests under a negative bias of −1000 V at 65 °C. For comparison, the K^0 center density of the SiN_x film is also shown. The data points represent the mean values for data obtained at three measurement points, and the error bars correspond to the standard deviation of the mean.

behavior also supports our hypothesis.

We assumed that the saturation of P_{max} is realized when Q_f is saturated; however, it is also possible that P_{max} saturates before the K centers in the SiN_x layer are completely charged. The saturation current densities of diodes depend on the surface band bending, and tend to saturate when the surface band bending approaches deep depletion. If the surface of the p^+ emitter reaches deep depletion before the saturation of Q_f in the front SiN_x layer, the saturation value of P_{max} should therefore be determined by not the total density of K centers but the saturated saturation current density.

The thermally grown SiO_2 films underlying the SiN_x films may play an important role in the charge accumulation process. In a previous study on the corona charging of SiN_x films,[37)] externally injected positive charges in SiN_x films directly deposited on c-Si substrates dissipated via charge transfer between the SiN_x films and the substrates, sometimes within 10 min. Thin SiO_2 films have been reported to prevent such charge transfer when inserted underneath the SiN_x films.[36,37)] In this context, the SiO_2 films in our n-type PERT cells may therefore help the SiN_x films retain their additional positive charges. It is also likely that the PID behavior will be changed by modifying the SiO_2 film properties, such as thickness and film density, by removing the SiO_2 film, or by exchanging it for another film, such as Al_2O_3.[38)]

To further confirm our proposed mechanism, we attempted to observe the saturation behavior of the positive charge density using C–V measurements. The obtained values were compared with the K center density measured by ESR. In this experiment, we used cell-level

PID tests in which module-like layer stacks composed of glass/EVA/cell were stressed[27,28] to obtain PID-affected unlaminated samples. The tests were performed under a constant negative bias of −1000 V at a constant temperature of 65 °C. Such a low temperature was required to avoid the unfavorable lamination of the sample stacks. *C*–*V* measurements were obtained for the SiN_x/SiO_2/p-type c-Si/Al sample, and a mercury probe was used as the front contact. Figure 7 shows Q_f values before and after PID tests for 1.5 and 3 h and the density of K^0 centers measured by ESR. The initial Q_f was ∼2×10^{12} cm^{-2}. Q_f increased to ∼7×10^{12} cm^{-2} and became saturated after the cell-level PID test for 1.5 h. Comparison with reported data[15,28] revealed that the degradation rate in the cell-level PID test at 65 °C was about 90 times lower than that in the module-level PID tests at 85 °C. The cell-level PID test for 1.5 h therefore corresponds to the module-level PID test for 60 s. As shown in Fig. 2, the degradation of the PV modules was strongly saturated within 60 s, which implies that the saturation of $P_{max}/P_{max,0}$ originates from that of Q_f. The saturation value of Q_f was 7×10^{12} cm^{-2}, which is of the same order as the density of K^0 centers (4×10^{12} cm^{-2}). Note that the total density of K centers was greater than the measured K^0 density because the total density also includes the densities of K^- and K^+ centers. The total densities of K centers are known to be one order of magnitude greater than those of K^0 centers.[33] The above findings are consistent with our hypothesis that the origin of the positive charges is the extraction of electrons from K centers.

Note that there was uncertainty in the above investigation based on *C*–*V* and ESR measurements. *C*–*V* measurements generally underestimate charge densities because the charges are assumed to be present at the insulator/semiconductor interface. Moreover, in our measurements, all the *C*–*V* curves showed clockwise hysteresis, indicating electron injection from the front electrode. (In the sample, hole injection was probably effectively prevented by the SiO_2 film underneath the SiN_x film.) This caused negative-bias instability and led to the further underestimation of Q_f. As for the ESR measurement, ESR can only detect K^0 centers, leading to the underestimation of the total density of K centers. To identify the actual total density of K centers, ESR combined with ultraviolet-light irradiation has to be employed.[33] Therefore, additional work is required to clarify the actual relationship between Q_f and the density of K centers.

5. Conclusions

Through rapid PID tests, we investigated the progression of PID in n-type PERT cell modules. In the PID tests in which a negative bias of −1000 V was applied at 85 °C, we found that PID occurred within 5 s and was strongly saturated within 60–120 s. This very rapid degradation implies that PID in n-type FE c-Si PV modules is caused by positive charge accumulation in the front passivation films. The rapid degradation and its subsequent saturation can both be consistently explained by assuming that positive charge accumulation originates from the K^+ centers formed by the extraction of electrons from K^0 and K^- centers.

To test this model, we investigated the dependence of the progression of PID on applied bias by using an increased bias of −1500 V. The degradation rate depended on the applied bias; conversely, the saturation value of $P_{\mathrm{max}}/P_{\mathrm{max},0}$ was independent of the applied bias, implying that the positive charge density was limited to a certain maximum value. We also conducted regeneration tests on modules subjected to PID tests for different durations by applying a positive bias of +1000 V at 85 °C. The progression of the regeneration behavior was independent of the duration of the degradation tests, which also implies a limited positive charge density. These results are consistent with our proposed model.

To further test our model, we performed C–V and ESR measurements on a $\mathrm{SiN}_x/\mathrm{SiO}_2$/p-type c-Si/Al sample subjected to cell-level PID tests. We observed the saturation behavior of Q_f in the insulator film equivalent to that of P_{max} of the modules. The saturation value of Q_f was of the same order as that of the K^0 center density measured by ESR. This finding further supported our proposed model. However, there was uncertainty in the values of Q_f and K center density. More accurate results are therefore required to clarify the actual relationship between Q_f and K center density.

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